HIGH PRESSURE BINARY MASS DIFFUSION COEFFICIENTS FOR COMBUSTION ENGINEERING APPLICATIONS AND SENSITIVITY STUDY FOR DROPS IN ZERO GRAVITY

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ABSTRACT

A model for high pressure binary diffusion coefficient calculation is proposed based on considerations originating from re-casting both the low pressure kinetic theory and the Stokes-Einstein infinite dilution expressions into forms consistent with corresponding states theory. These considerations lead to an ansatz that is an expression reflecting departures from the kinetic theory relationship through a division factor that is a function of the reduced species density and that becomes unity in the limit of low pressure gases. Available high pressure data sets extracted from the literature are used to derive correlations for the factor that are eventually categorized according to the species system. The typical uncertainty in these correlations is estimated as 10 to 15 %, with a maximum uncertainty of about 30% for the high density regime. Further, simulations of heptane drops in nitrogen under zero gravity and at high pressure conditions are performed to investigate the sensitivity of the drop diameter predictions to this typical range of uncertainty in the prescribed diffusivity. Results show that the RMS deviation variation in the drop diameter value is approximately a factor of four less than the corresponding imposed change in the diffusivity. The consequences of this finding on future comparisons between microgravity data and simulations are discussed in the context of determining from this comparison the thermal diffusion factor.

1 Introduction

The modeling of combustion phenomena occurring in Diesel, gas turbine and liquid rocket engines requires the accurate knowledge of mass diffusion, D_{ij}, and thermal diffusion, α_{Tij}, coefficients. This is because despite the turbulent environment in the combustion chamber, at supercritical conditions the species molecular transport governs the dissipation (irreversible entropy production) and backscatter, as shown in recent study [1]. In fact, the dominating effect in the dissipation is that associated with the Fick's diffusion terms, with significant contributions from the multiplied Fick's and Soret (i.e. thermal diffusion) terms. This is in sharp contrast to atmospheric flow turbulence, where viscous effects dominate. Despite the wide range of combustion applications, there are no systematic studies devoted to the modeling of molecular diffusion at high pressure conditions [2]; the same situation prevails for thermal diffusion effects [2]. If high pressure D_{ij} models were available, microgravity experiments with free single-component drops in pure species surroundings could be pivotal in initiating the determination of α_T's from comparison of drop diameter timewise variation, $d(t)$, data and numerical predictions, because the only unknown transport coefficient would be α_T (reliable thermal conductivity, λ, and viscosity, η, high pressure models do exist [3]).

Although kinetic theory (KT) gives a firm theoretical basis for low pressure diffusion coefficient expressions (dilute gases), there is not a similar basis for high pressure dense gases or liquids. Since high pressure fluids can have reduced densities, $\rho_r \equiv \rho/\rho_c$ (the subscript c denotes the critical point), comparable to those of liquids, it may be pertinent to also inquire about typical liquid diffusion calculations. Infinite dilution diffusion in liquids is usually depicted by extending the Stokes-Einstein (SE) hydrodynamic model for motion of very small particles in a liquid down to the molecular size level, but the resulting correlations have only mixed success ([3], [4], [5], [6], [7]). At a minimum, diffusion coefficient correlations should be dimensionally consistent; moreover, in conformity with results for other transport properties such as η and λ, adherence to the principle of corresponding states is deemed appropriate. In this connection, the temperature, T, and ρ (but not the pressure, p) are here considered as the relevant primitive variables in correlations since the pure species critical values are closely related to characteristic molecular interaction potential and size. Pressure enters the calculations through the equation of state (EOS); mole fractions, X_i, or mass fractions enter through appropriate mixing rules. Particular species of interest include H_2, He (as a safe alternative to H_2 in experiments), O_2, N_2 (used in microgravity experiments, and also needed to model air), alkane

hydrocarbons, C_nH_{2n+2}, as representative fuels, and the products of combustion H_2O and CO_2.

In this study we first present existing low p information in terms of corresponding states forms, as a precursor to establishing the strategy for developing a high p relationship. This relationship is next presented and used for binary species correlations based on a multitude of experimental data. Furthermore, given the acknowledged experimental and resulting correlation errors, a numerical sensitivity study is conducted in the realm of isolated single-component drops in high p pure-species fluid under zero gravity. The purpose of this study is to determine for a fixed value of α_T, the range of variation of $d(t)$ with D_{ij}, which is chosen within the uncertainty of the correlation. The results of this sensitivity study are interpreted in the frame of comparisons between microgravity data and numerical predictions for the purpose of determining α_T values.

2 Low pressure relationships

2.1 Gases

Low p KT theory has been discussed in [8] and in [9] for combustion applications. The lowest order expression for the binary diffusion coefficient from KT is ([3], [6])

$$(D_{ij})_{KT} = 3(kT/(2\pi m_{ij}))^{1/2}/[8n\sigma_{ij}^2\ \Omega_D(kT/\varepsilon_{ij})] \tag{1}$$

where i and j are species indices, k is the Boltzmann constant, m_{ij} is the reduced mass, n is the (average) molecular number density, σ_{ij} denotes the collision diameter and Ω_D is the diffusion collision integral in terms of temperature referenced to collision potential scale, ε_{ij}. Parameters σ_{ij} and ε_{ij}, along with the form of the function Ω_D are empirically determined; η measurements are a major source of parameter values for $i = j$.

For a pure substance with $kT \leqslant \varepsilon_{ii}$, in terms of the viscosity integral Ω_v, the η dependency on σ_{ii} and ε_{ii} is [3]

$$\eta^{-1} \sim \sigma_{ii}^2\Omega_v(kT/\varepsilon_{ii}) \sim \sigma_{ii}^2\sqrt{(\varepsilon_{ii}/k)}, \tag{2}$$

offering a way to determine $\sigma_{ii}^2\sqrt{(\varepsilon_{ii}/k)}$. ¿From the corresponding states rules [3],

$$\sigma_{ij} \sim (V_{c,ij}/N_A)^{1/3} \text{ and } \varepsilon_{ij} \sim kT_{c,ij} \tag{3}$$

where N_A is Avogadro's number, and the pseudocritical parameters are $V_{c,ij} = [(V_{c,i})^{1/3} + (V_{c,j})^{1/3}]^3/8$ and $T_{c,ij} = \sqrt{(T_{c,i}T_{c,j})}$, where V is the molar volume. Using these rules in a relation similar to eq. 2, the

empirical value of $\sigma_{ij}^2\sqrt{(\varepsilon_{ij}/k)}$ is herein replaced by $6.0 \times 10^{-3} r_v (V_{c,ij})^{2/3}\sqrt{T_{c,ij}}$, with the expectation of $r_v \simeq$ constant. The r_v being constant is supported by σ_{ij} and ε_{ij} data from [10] for collisional interactions for five noble gases, air, and nine simple polyatomic gases: except for interactions with He (where $r_v \cong 0.95$), the data are consistent with $r_v = 1.0$ to within $\simeq 2\%$ error or less. Further examination of the data reveals that aside from collisional interactions with the noble gases, $kT_{c,ij}/\varepsilon_{ij} \cong 1.27$ to within an error of $\simeq 5\%$ or less. (The ratio is closer to 1.05 for He and 1.17 for Ar.) The following replacements

$$\sigma_{ij} = 0.692(V_{c,ij}/N_A)^{1/3} \text{ and } \varepsilon_{ij} = kT_{c,ij}/1.27 \tag{4}$$

thus give accurate scaling of transport parameter values (e.g. for η) and a good estimate of T scaling for the collision integrals.

Using the collision integrals of [10] for $1 \leqslant kT/\varepsilon_{ij} \leqslant 10$, augmented by Lennard-Jones functions [3] for $kT < \varepsilon_{ij}$, Ω_D is here fitted as

$$\Omega_D = 1.20(T_{c,ij}/T)^s \tag{5}$$

where $\ln(s) = \sum_{m=0}^{5}[a_m(ln(T/T_{c,ij}))^m]$, with a_m = {-0.84211, -0.32643, -0.10053, 0.07747, 0.0127, -0.00995} for $0.2 \leqslant T/T_{c,ij} \leqslant 10$. If $T > 10T_{c,ij}$, s is here taken as a constant, 0.2304, which is its value at $10T_{c,ij}$. Generally, s takes values between about 1/4 to 1/2.

The final corresponding states expression for the low p binary diffusion coefficient is

$$(D_{ij})_{KT} = 2.81 \times 10^{-5} V[(m_i^{-1} + m_j^{-1})T]^{1/2}(T/T_{c,ij})^s/(r_D V_{c,ij}^{2/3}) \qquad \text{in } cm^2/s \tag{6}$$

where m_i, m_j are molar masses ($g/mole$), T is in K, and V in $cm^3/mole$. The factor r_D is a constant parameter of $O(1)$, used as an empirical adjustment for the particulars of the collisional interaction of a given pair of species. (This is especially needed for non-simple species.) Values of r_D, as obtained from diffusion data at $p = 1atm$ given by [11], [3] and [12], are listed in Table 1. (Note: $V = 82.056T$ at $p = 1atm$.) The light species He and H_2 behave in a similar manner, as does benzene (C_6H_6) and acetone (C_3H_6O). Unfortunately, the amount and quality of data related to the heavier alkanes is less than desirable. Overall, errors in values of D_{ij} for low p gases (see in Table 1) are of order 5%; the same conclusion is reached by [10].

2.2 Liquids

For liquid solvents with moderate η ($\eta \leqslant 0.1$ poise), the infinite dilution (i.e. $X_i \longrightarrow 0$) binary diffusion coefficients, D^o_{ij}, are frequently expressed using the SE formula ([3]):

$$D^o_{ij} = kT/(\eta_j l_{ij}) \tag{7}$$

where l_{ij} is a characteristic scattering length of solute i in solvent j. An empirical correlation with lowest error is that due to Tyn and Calus [13], appropriately modified by [3]

$$l_{ij} = 1.546 \times 10^{-7} (\sigma_{b,i}/\sigma_{b,j})^{0.15} V_{b,i}^{0.4333}/V_{b,j}^{0.2667} \text{ in } cm \tag{8}$$

where σ_b is surface tension ($dynes/cm$) and subscript b indicates the normal boiling point temperature, T_b. The average expected error with this expression is about 10% and the maximum error is about 30%. Although the modified expression is more straightforward than the original one involving parachors, the need to find σ_b and V_b is inconvenient. The present strategy is to use corresponding states principles and replace $\sigma_{b,i}^{0.15} V_{b,i}^{0.4333}$ by $0.69 r_s T_{c,i}^{0.15} V_{c,i}^{1/3}$. Data [3] then shows that $r_s = 1.0$ for N_2, O_2, benzene, toluene, naphthalene and the alkanes (for n = 4 - 16); $r_s = 0.95$ for H_2O, 1.1 for H_2, and 0.88 for He. (A dimer should be used with water solutes [13], and thus the effective r_s value is 1.28) The dependency on the solvent in the form $\sigma_{b,j}^{0.15} V_{b,j}^{0.2667} \equiv 4.88\beta_j$ could also be expressed in terms of T_c and V_c; however, an expression in terms of the acentric factor, ω, is sought herein because of easy extension to mixtures. For a pure substance, the correlation $\beta = (\omega + 0.45)^{0.4125} + 0.27 X_A$ holds with $X_A = 1.0$ for alkanes (n = 6 - 16), benzene and toluene, and with $X_A = 0$ for non-hydrocarbons. This expression is easily extendable to solvent mixtures through a mole fraction average acentric factor, along with the alkane mole fraction in the mixture, X_A. The scattering length expression becomes

$$l_{ij} = 2.19 \times 10^{-8} r_s T_{c,i}^{0.15} V_{c,i}^{1/3}/\beta_j \tag{9}$$

with $r_s = 1.0$ for most solutes. Along with r_s, details of our β fit give for certain solvents an additional multiplier of 1.08 (H_2O), 0.91 (H_2), or 1.04 (He). However, liquid solvents with any of these species as a major constituent are not of interest. According to [3], for normal paraffin (alkane-alkane) solutions, an expression due to Hayduk and Minhas (see [3]) should be used instead of that in [13]. Calculations with this alternative expression for carbon numbers n = 7 - 16 and 300 K$\leqslant T \leqslant$ 370 K lead to a solvent function dependent on its reduced temperature, $T_r \equiv T/T_c, \beta_j = a T_r^{-b}$ where $a = 1 - \omega_j/3$ and $b = 1.17\omega_j/\omega_i^{0.41}$.

For species of interest, values from our proffered eq. 9 for l_{ij} deviate from the originals by about 3% or less, well within the accuracy of the SE correlation. This new expression is more convenient than the originals, may be used when properties at T_b are not available (e.g. CO_2), and may readily be applied to solvents that are not pure (i.e. mixtures). Note that solvent molecular association has not been considered in this discussion; it is not expected to be important for species combinations of interest [14].

It is well known ([15], [16], [3], [5], [17]) that for binary mixtures, the effective diffusion coefficient is $\alpha_D D$ ($D_{ij} = D$ for $i, j = 1, 2$) where $\alpha_D = 1 + X_k \partial(\ln \phi_k)/\partial X_k$ is the mass diffusion factor, ϕ_k is the fugacity coefficient, and k denotes either species, i or j. Given expressions for the D^o_{ij}'s, the liquid binary coefficient may be obtained from the Vignes rule ([3], [17]) through

$$\ln(D_{ij}) = X_j \ln(D^o_{ij}) + X_i \ln(D^o_{ji}). \tag{10}$$

Since for low p gas, there is no distinction between D_{ij} and D^o_{ij} (see that eq. 1 is independent of X_i or X_j), the same rule applies.

Note that $\alpha_D = 1$ in the infinite dilution limit; measurements involve a small but finite trace amount of solute into a carrier solvent and deviations from 1 are usually neglected. In fact, α_D measures departures from mixture ideality: for low p ideal gas, $\alpha_D = 1$, however, for liquids α_D may differ substantially from 1 (e.g. see examples in [17]). Since $\alpha_D = 0$ at the critical point ([15], [5]), there is an ambiguity in the value of α_D when the solvent is near (T_c, ρ_c). This fact, combined with the lack of accuracy in near-critical-point V values calculated from common EOS models ([3]), leads to a difficulty in the use of infinite dilution data for nearly critical solvents.

3 Modeling of high pressure diffusion coefficients

To correlate high p diffusion coefficients, the issue is the choice of a proper extension of the low pressure models to high p. Two extensions can be pursued: modify either the KT approach or the SE expressions. Since ρ is the primitive variable, it is ρ_r that is the pertinent correlation quantity at high p. As an illustration of correlations based on ρ_r rather than p_r, the data of [18] feature N_2, Ar and CH_4 as trace species in He at $p = 1$ - 6 MPa ($p_r > 4$) and $T = 248$ - 323 K ($T_r \gg 1$); however, $\rho_r = V_c/V \leq 0.16$ is not large. The data and $(D_{ij})_{KT}$ match to within 3% (other data for trace CO_2 is not as close). A literature search shows that available data for dense gas diffusion is for $\rho_r \leq 2$, whereas for most liquids $\rho_r \geqslant 2$ (at normal boiling, liquid

$\rho_r \approx 2.5$). Moreover, generally $T_r < 1$ for liquids, while $T_r \geqslant 1$ for dense vapors. These comparisons suggest that dense vapor diffusion correlations should be referenced to the KT expression, not a SE type formula, particularly since as mentioned above, SE does not hold for very high η solvents; indications are that it also does not hold in the low η limit ([5], [19]) or at ρ 's below critical ([20], [4]). Although some success has been obtained with SE based formulas for non-liquid systems with moderate η ([4], [7]), the idea here is to modify $(D_{ij})_{KT}$ from eq. 6 by a factor $w_D = 1 + \delta_D$ where δ_D is a function of the solvent ρ_r with $\delta_D \longrightarrow 0$ as $\rho_r \longrightarrow 0$

$$D^o_{ij} = (D_{ij})_{KT}/w_{D,j}, \tag{11}$$

rendering this expression valid for all ρ_r's; this expression is consistent with hard sphere scattering theory ([5], [20]). The ansatz is that the δ_D dependency on ρ_r and T_r is simple (generic), with only a few constant parameters involved. The protocol of determining the value of w_D is to use D^o_{ij} data in conjunction with calculated $(D_{ij})_{KT}$ from eq. 6, and obtain $\delta_D(\rho_r)$ from eq. 11. Note that at fixed (high) ρ, data indicates a weak dependence of diffusivity on T ([21], [5], [4]). Similarly, η is mostly ρ dependent ([4], [5]), so there is no advantage to using η as a correlation variable over ρ_r.

An example of the proposed ansatz for dense gases uses the data of [23] for light trace species (H_2, He) in N_2 or Ar carrier species; p = 272 -1360 atm (27.6 - 132 MPa), T = 298 K and $0.85 \leq \rho_r \leq 2.0$. A very good fit to the data is with $\delta_D = c\rho_r^{3/2}$, where $c = 0.42$ for He in Ar and $c = 0.58$ for the other pairs. Figure 1 depicts the w_D data and fit curves. Note that $T_r \geqslant 2$, so that the critical point is avoided. Fit deviations are at most 10% and usually lower; the dependency on ρ_r is accurately captured. The measurement error estimate [23] is $\simeq$ 5% (or slightly larger).

Other data in [23] feature He as the carrier with N_2, Ar, CF_4, and alkanes with carbon number n = 1 to 4 as solutes. The carbon based solutes display a decrease in the value of w_D at larger ρ_r and δ_D is maximum at $\rho_r \approx$ 1.2 -1.3. The w_D calculated (values and fits in Fig. 2) from D^o_{ij} data yield $\delta_D \cong c\rho_r^{0.83}$ for the ascending part of the curves, with $c = 0.18$ for N_2 and Ar, $c = 0.27$ for CH_4, $c = 0.23$ for C_2H_6, and $c = 0.20$ for $n = 3$ or 4 (for $n = 3$, r_D =1.02 in eq. 6). For the descending part of the alkane curves, $\delta_D \cong (c + \Delta c)\rho_r^{0.83}$, with $\Delta c = 0.48 - 0.39\rho_r^{0.83}$ for $\rho_r \geqslant 1.284$ ($p \geqslant 75$ MPa), changing the ρ_r dependency for those parts of the curve. Figure 2 also illustrates the w_D values for CF_4, assuming $r_D = 1$. The w_D values and fit for solutes N_2 and Ar are given in Fig. 3, along with data for benzoic acid in CO_2 (the data is from [20] with $r_D = 3/4$ estimated from the diffusivity at ρ_c; see Fig. 2 in [20]). The scatter in Fig. 3 ($\simeq$ 10% or

less) is typical for high ρ measurements. Data fits are thus somewhat ambiguous; the emphasis is here on capturing data trends in the context of using generic expressions, rather than the most accurate portrayal of values for a specific data set or species pair. Considering both data scatter and the different character of solvent-solute pairs, the Fig. 3 curves are consistent with the proposed ansatz.

Umezawa and Nagashima [22] present data for $p \simeq 10$ MPa with CO_2 as solvent and alkane solutes with carbon number $n = 5$ - 14. This data is for $T_r \approx 1$ and $1.56 \leq \rho_r \leq 1.75$. Although of considerable potential interest, use of this data faces difficulty due to lack of r_D values and possible question as to data accuracy ([7]). However, if $r_D \sim \omega^{-1/2}$ (ω of the alkane), then the data sets of [22] nearly overlap. This type of behavior for long chain molecules is not totally implausible ([5]); with the added assumption $r_D \cong 0.9$ for $n = 5$, the range of w_D values generally coincide with that in Fig. 2, although w_D increases strongly with ρ_r, not duplicating the dependency of Fig. 2 curves. Therefore, no conclusive results may be obtained with this data.

A recent comprehensive review of available high ρ diffusion data is that of [19]. About 80% of the data is for CO_2 as the solvent. Much of the available data is for species that are not of primary interest for our ultimate purpose (highly polar species, esters, alcohols, etc.) and even when of interest, it is restricted to solvent $1.0 \leq T_r \leq 1.1$, with lower values dominant (see also [20]). Unfortunately, as noted before, this leads to possible difficulty in use of the data due to potential accuracy problems with V values, and also due to ambiguity in the values of α_D (not being 1). This is unfortunate since Liu and Ruckenstein [7] show that when the chemical potential effect is considered in the diffusion coefficient (equivalent to our $\alpha_{Dij} D_{ij}$), the correlation of data is much improved. Difficulties in accurate ϕ and α_D calculations, especially for near critical solvents and/or polar species, are discussed in Chapter 5 of [14]. The effect of α_D values for benzene in CO_2 is discussed in detail by [15], [16] who make rough estimates of α_D based on Peng-Robinson or BWR EOS; large variations in $\alpha_{Dij} D_{ij}$ are possible for $p < 10$ MPa ($\rho_r \lesssim 1$). These variations depend strongly on both the trace mole fraction and binary interaction parameter used in the EOS. The [15], [16] studies show that there is an injected quantity of solute threshold ($\simeq 1 \mu l$ in their experiment) above which reduction of α_D below 1 is estimated to be significant, which may lead to some very small measured D^o_{ij}.

Figure 4 presents w_D values for trace acetone in CO_2 calculated using data from [4], [22] and [24]. In [24] the injected quantity is $0.5 \mu l$ and our estimated solute threshold is lower by a factor of $\simeq 2$ compared with [15], [16] because the CO_2 flow rate is lower by the same factor. Only data for $p \geqslant 9$MPa are used from [24]

since data fitting error and ρ fluctuations are large at lower p's. The variation of δ_D for $\rho_r > 1.5$ (see Fig. 4) is well described by the curve $\delta_D = 0.05\rho^{3.2}$.

One relevant species pair for which there is considerable amount of data available is benzene in CO_2. The w_D results are presented in Fig. 5. Data from [16] is for 0.7 μl of injected solute and $p > 9$ MPa. The effect of injected quantity of solute on measured D_{ij}^o is exhibited in [4] and [15]. The scatter is large: as much as 15% for one data set at given ρ_r and T_r, and even larger across data sets. Curve $\delta_D = 0.06\rho_r^{3.2}$ emulates the variation for acetone in CO_2, whereas $\delta_D = 0.23\rho_r^{0.83}$ emulates the variation with He as the solvent (Figs. 2 and 3). For $\rho_r > 1$, the variation (but not the value) of w_D for each of the diverse data sets roughly corresponds to one of these curves. The mean variation is thus approximately $\delta_D \approx 0.12\rho_r^2$. The unreasonably large w_D values for $\rho_r < 1$ result from data of [25]. Assumed accurate V values of CO_2, taken from the NIST Chemistry WebBook, were used in this calculation, however, reductions in V would decrease w_D and increase ρ_r. Also, if $\alpha_D \approx 0.7$, this would shift (multiply) the w_D values for $\rho_r < 1$ to lower values (the expected behavior). This is consistent with values of α_D estimated in [15]. Finally, it is possible that the data is in error. Using the SE expression to fit the data does not resolve the apparent discrepancy, as the resulting scattering length for $\rho_r < 1$ is similarly larger than that for $\rho_r > 1$. No significant correlation of w_D values with T_r is apparent, although $1 \leq T_r \leq 1.1$, making this lack of correlation subject to future scrutiny. Overall, the scatter could have a partial explanation if different amounts of trace benzene were used in the different data sets, possibly yielding diverse α_D values (below 1) and effective diffusivities. Obviously, more data, carefully obtained (especially at larger values of T_r), would be useful.

The last data sets to be examined involve hydrocarbons for both solvent and solute. Included are octene (C_8H_{16}) solute in solvents ethane (C_2H_6), propane (C_3H_8) and hexane (C_6H_{14}) from [26], octene in ethane from [27] and benzene (C_6H_6), toluene (C_7H_8) and naphthalene ($C_{10}H_8$) in hexane from [28]. Values of r_D are not available, hence only $r_D w_D$ is here determined. However, $r_D w_D$ values for octene in ethane or propane at smaller ρ_r suggest that $r_D \approx 2$; $r_D = 2$ is adopted here for all species pairs. The resulting values of w_D are plotted in Fig. 6, along with a 'reference' curve $w_D = [2 + \exp(-4.7\rho_r^3)]/3$ that qualitatively describes the overall behavior (most deviations $\lesssim 10\%$). The data indicate a negative δ_D with minimum $r_D w_D$ =1.0; the scatter in Fig. 6 could be considerably reduced with appropriate values of r_D or w_D at large ρ_r (e.g. for $r_D = 2$ as in Fig. 6, the asymptotic $w_D \simeq 0.9 - 0.8\omega_{solute}$). Having $r_D \approx 2$ is consistent with the asymmetric, non-simple hydrocarbon molecules becoming 'entangled' (steric effect), increasing the collision

cross–section, with consequent reduced diffusion. The decrease in w_D ($\delta_D < 0$) could possibly then result from a forced molecular alignment ('semi-crystallization') due to packing at the higher ρ's, leading to easier slippage of the solute molecules in the solvent. Note that octene in propane or hexane show a minimum in w_D in the vicinity of $\rho_r \approx 1.2$ -1.3; the other pairs show a leveling of w_D values at larger ρ_r. The appearance of a minimum mirrors the maximums of alkanes in He as shown in Fig. 2. Use of the SE expression to fit the data (for all r_s unity) yields a solvent $\beta = 0.64$ for octene in ethane ($\pm$10% scatter), 0.96 for octene in hexane ($\pm$7% scatter) and 0.80 for the other pairs ($\pm$15% scatter). Setting $r_s = 0.83$ for octene gives a consistent set of values, $\beta = 0.53$, 0.67, 0.80 for ethane, propane, hexane respectively. For a given fit, $\beta \propto (r_s)_{solute}$. These values are different from those of liquids, which would be near 1. The small β correspond to large r_D . The accuracy of this approach is not superior to the modified KT one, especially with optimized r_D and/or asymptotic w_D. Its main drawback is the lack of uniform validity for all values of ρ_r.

¿From the available data, the ansatz of a generic form for δ_D may apply for distinct classes of solvent-solute pairs, as follows:

When both solute and solvent are hydrocarbons, it appears that $r_D \approx 2$ and $w_D \leq 1$ (with a form similar to the reference curve of Fig. 6). It also seems possible that the (level) value of w_D for $\rho_r > 1$ may depend on solute molecular weight or ω; more data are required.

For other solvent-solute pairs, the form $\delta_D = c\rho_r^b$ where $c \sim b^{-s}$ with $s \approx 1$, seems adequate; no dependency on T_r is evident. For a light solute (H_2, He), the data is well fit for b =3/2; for H_2 in O_2 (rocket motor models), $c \simeq 0.58$. For a light solvent, $b = 0.83$ where $c \cong 0.20$ - 0.23 for hydrocarbon solutes (with a possible decrease at extreme p) and $c \cong 0.18$ for other solutes. For hydrocarbon solutes in air or combustion product solvents, reliance on the benzene in CO_2 data suggests that $\delta_D \approx 0.12\rho_r^2$. This is a crude estimate; however, for conditions of interest $\rho_r \leq 1$ and errors in w_D values will be relatively minor.

Lastly, for air or combustion products in hydrocarbons, no information is available. Fortunately, the solubility of these solutes in hydrocarbons is low and their mass fractions in a mixture will be quite small. Thus, errors from ignorance of δ_D values will probably have little effect on any model studies. For simplicity, convenience and caution (it is desirable to have minimal δ_D at large ρ_r), a linear $\delta_D \approx 0.2\rho_r$ may be used.

Data scarcity and scatter make this ansatz provisional. Clearly more data is needed, especially for solvents with T_r well above 1 (e.g. N_2). When the solute and/or solvent is a heavier hydrocarbon, more information on r_D values is also needed. Expected error in D_{ij} estimates is in the range 5 - 30%. Typical

errors are probably 10 - 15% or less. Finally, the information derived herein can be used for multicomponent mixtures, as mixing rules give relevant diffusivities in terms of the binary coefficients (e.g. [6]).

4 Sensitivity studies for drops in zero gravity

Given the expected error in D_{ij} estimates, it is important to understand the impact of this uncertainty on the numerical prediction of $d(t)$. To this end, several zero gravity calculations are here performed with the model of [31], [32], [33], which is valid for all p's. Because this model is well documented, and for brevity, the details of the formulation are not given herein. Displayed in Fig. 7 are results from calculations for heptane drops in N_2 (see initial conditions in caption) at $p = 1$ MPa for several multipliers of D (0.7, 1.0, 1.1 and $1.5 \cong 1/0.7$); calculations at 2 MPa (results not shown) showed similar trends. If the curve for $1.0 \times D$ is considered as the reference curve, the RMS deviation of the drop radius, R_s, for all other values of D is 0.099, 0.025 and 0.118 for the multipliers 0.7, 1.1 and 1.5. This shows that the uncertainty in the R_s value is less (by $\simeq$ a factor of 4) than that on the D value. Since outside the heptane drop $\rho_r \lesssim 0.2$, this regime is near the KT range and most of the error can here be traced to the uncertainty in the value of r_D ($\sim 8\%$). Considering the ratio of D to R_s uncertainties, this implies a corresponding R_s uncertainty of $\simeq 2\%$.

For future comparisons of simulations of single-component drops in pure fluid species with equivalent high p microgravity d data, two scenarios in determining α_T are possible for given D. If the simulations show little sensitivity to the value of α_T when compared to the data, then the measured d is mostly sensitive to other factors. In this case, the uncertainty in the value of α_T might be large, but the importance of thermal diffusion will be small. However, if the simulations show large variations with α_T, then the measured d is strongly dependent on α_T, whose value may be determined with relative accuracy. Since in general $\alpha_T(X_i, T)$ at specified p, this single α_T value would represent a first (but important) step in finding α_T.

5 Summary and conclusions

An ansatz for a calculating high pressure diffusion coefficients has been derived by recasting low pressure gas relationships in a corresponding states form, which is extended at high pressures through a general dependency on the reduced density. Using available data from the literature, correlations were obtained, yielding specific dependencies on the reduced density for different classes of binary species systems. Typical

errors in these correlations are $\simeq$10 - 15%, and with a range of 5 - 30%. The sensitivity of high pressure drop simulations to the uncertainty in the diffusion coefficient data has been determined, as a first step towards comparisons of simulations with microgravity drop diameter/radius data. It has been shown that when thermal diffusion effects are important, the knowledge of the binary diffusion coefficients within the correlation uncertainty allows a relatively accurate determination of the binary mixture thermal diffusion factor.

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References

[1] Okong'o, N. and Bellan, J. "Direct Numerical Simulation of a transitional supercritical mixing layer: heptane and nitrogen" submitted for publication to J. Fluid Mech. (2000)

[2] Rosner, D., Transport Processes in Chemically Reacting Flow Systems, Dover Publications, 2000

[3] Reid, R. C., Prausnitz J. M. and Poling, B. E., The Properties of Gases & Liquids (4th edition), McGraw-Hill Book Co., NY, 1987

[4] Sassiat, P. R., Mourier, P. Caude, M. H.and Rosset, R. H., Anal. Chem. 59:1164 (1987)

[5] Liong, K. K., Wells, P. A. and Foster, N. R., J. Supercrit. Fl. 4(2):91 (1991)

[6] Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., Molecular Theory of Gases and Liquids, John Wiley and Sons, NY, 1954

[7] Liu, H. and Ruckenstein, E., Ind. Eng. Chem. Res. 36:888 (1997)

[8] Ern, A. and Giovangigli, V., Phys. Rev. E. 53(1):485 (1996)

[9] Paul, P. and Warnatz, J., Proc. Comb. Inst. 27:495 (1998)

[10] J. Bzowski, J. Kestin, E. A. Mason and F. J. Uribe, J. Phys. Chem. Ref. Data 19(5):1179 (1990)

[11] Maynard, V. R. and Grushka, E., Adv. in Chromatogr. 12: 99 (1975)

[12] Taylor, W. L., Hurly, J. J., Meyer, B. A. and Dunlop, P. J., J. Chem. Phys. 103:6959 (1995)

[13] Tyn, M. T. and Calus, W. F., J. Chem. Engr. Data 20(1):106 (1975)

[14] Prausnitz, J. M., Lichtenthaler, R. N. and de Azevedo, E. G., Molecular Thermodynamics of Fluid-phase Equilibria (2nd edition) Prentice-Hall Inc., Englewood Cliffs, NJ, 1986

[15] Ago, K. and Nishiumi, H., Ind. Eng. Chem. Res. 37:1692 (1998)

[16] Ago, K. and Nishiumi, H., J. Chem. Engr. Japan 32(5):563 (1999)

[17] Vignes, A., Ind. Eng. Chem. Fundam., 5(2):189 (1966)

[18] Hu, A. T.-C. and Kobayashi, R., J. Chem. Engr. Data 15:328 (1970)

[19] Suarez, J. J., Medina, I. and Bueno, J. L., Fl. Phase Equilibria 153:167 (1998)

[20] Catchpole, O. J. and King, M. B., Ind. Eng. Chem. Res. 33:1828 (1994)

[21] Suarez, J. J., Bueno, J. L. and Medina, I., Chem. Engr. Science 48(13):2419 (1993)

[22] Umezawa, S. and Nagashima, A., J. Supercrit. Fl., 5(4):242 (1992)

[23] Balenovic, Z., Myers, M. N. and Giddings, J. C., J. Chem. Phys. 52(2):915 (1970)

[24] Funazukuri, T., Kong, C. Y. and Kagei, S., Int. J. Thermophysics 21(3):651 (2000)

[25] Swaid, I. and Schneider, G. M., Ber. Bunsenges Phys. Chem. 83:969 (1979)

[26] Eaton, A. P. and Akgerman, A., Ind. Eng. Chem. Res.36:923 (1997)

[27] Noel, J. M., Erkey, C., Bukur, D. B. and Akgerman, A., J. Chem. Eng. Data 39(4):920 (1994)

[28] Sun, C. K. and Chen, S. H., Chem. Eng. Science 40:2217 (1985)

[29] Funazukuri, T., Ishiwata, Y. and Wakao, N., AIChE J. 38:1761 (1992)

[30] Levelt-Sengers, J. M. H., Deiters, U. K., Klask, U., Swidersky, P. and Schneider, G. M., Int. J. Thermophysics 14:893 (1993)

[31] Harstad, K. and Bellan, J., Int. J. of Multiphase Flow, 26(10):1675 (2000)

[32] Harstad, K. and Bellan, J., Combustion and Flame 124:535 (2001)

[33] Harstad, K. and Bellan, J., "Evaluation of commonly used assumptions for isolated and cluster heptane drops in nitrogen at all pressures", accepted for publication in Combustion and Flame 126 (2002)

Specie pairs	Constant	Approx. error
$He - H_2$	0.86	+0.005, -0.01
$He - O_2$	0.93	+0.03, -0.01
He,$H_2 - N_2, Ar$	0.93	+0.03, -0.02
$He, H_2 - CH_4$	0.92	+0.02, -0.02
$He, H_2 - C_2H_6$	1.0	
$He, H_2 - C_4H_{10}$	1.045	+0.015, -0.04
$He, H_2 - C_5H_{12}, C_6H_{14}$	1.1	+0.1, -0.1
$He, H_2 - CO_2$	0.96	+0.02, -0.02
$He, H_2 - H_2O$	0.82	+0.01, -0.02
$N_2 - O_2$	0.92	+0.01, -0.01
$N_2, O_2 - H_2O$	0.82	+0.0, -0.02
$CO_2 - H_2O$	0.93	+0.01, -0.03
$N_2 - CO_2$	0.89; 1.0	[6; 3 points]
N_2, Ar – Alkane (n = 4-6)	1.0	+0.08, -0.08
$N_2 - C_6H_6, C_3H_6O$	1.02	+0.03, -0.02
$Ar - C_6H_6, C_3H_6O$	0.87	+0.04, -0.02
$CO_2 - C_6H_6, C_3H_6O$	0.90	+0.02, -0.04

Table 1: Diffusivity Normalization Constants.

Figure Captions

Figure 1. w_D vs. $\rho_r = V_c/V$ for light solutes. Data from [23]: ◯ for $N_2 - H_2$; □ for $N_2 - He$; △ for $Ar - H_2$; ▽ for $Ar - He$. Curves for $\delta_D = c\rho_r^{3/2}$, $c = 0.42$, 0.58, see text.

Figure 2. w_D vs. $\rho_r = V_c/V$ for carbon based solutes in He. Data from [23]: ▽ for CH_4; △ for C_2H_6; ◯ for C_3H_8, C_4H_{10}; □ for CF_4. Curves for $\delta_D = c\rho_r^{0.83}$ with variable c, see text: $- \cdot -$ corresponds to ▽; $- - -$ corresponds to △; —— corresponds to ◯.

Figure 3. w_D vs. $\rho_r = V_c/V$ for N_2 and Ar in He, benzoic acid in CO_2. See text for data sources: ◯ for $He - N_2$; □ for $He - Ar$; ▽ for $CO_2 - C_7H_6O_2$. Curve is for $\delta_D = 0.18\rho_r^{0.83}$.

Figure 4. w_D vs. $\rho_r = V_c/V$ for acetone in CO_2. Data sources: [24] ◯ for $T = 308.2K$, □ for $T = 313.2K$; [4] △; [22] ▲. Curve is for $\delta_D = 0.05\rho_r^{3.2}$.

Figure 5. w_D vs. $\rho_r = V_c/V$ for benzene in CO_2. Data sources: [25] ◯; [4] ▽; [30] △; [21] □; [22] ▼; [29] ▲; [16] ◇. Dashed curve is for $\delta_D = 0.23\rho_r^{0.83}$. Solid curve is for $\delta_D = 0.06\rho_r^{3.2}$.

Figure 6. w_D vs. $\rho_r = V_c/V$ for hydrocarbon solvents and solutes, $r_D = 2$. See text for data sources and equation of reference curve. ◇, ♦ ethane - octene (♦ is data from [27]), □ propane - octene, ■ hexane - octene, ▽ hexane - benzene, △ hexane - toluene, ◯ hexane - naphtalene.

Figure 7. Drop radius versus time for a heptane drop in N_2 as a function of the diffusivity used in the calculation. Initial conditions are: $R_s^0 = 6 \times 10^{-3} cm$, $T_d^0 = 325K$, $R_e^0 = 5 \times 10^{-2} cm$, $T_e = 800K$, $p_e = 1MPa$, where the subscript e stands for the far field condition. $- \cdot - 0.7D$; —— $1.0D$; $- - - 1.1D$; $- \cdot - \cdot - 1.5D$.

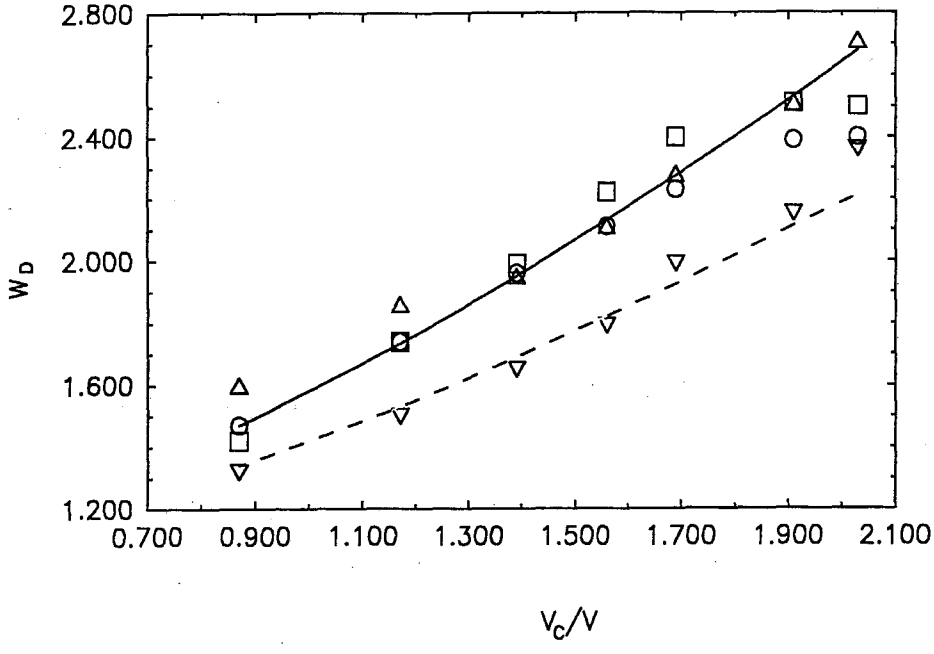
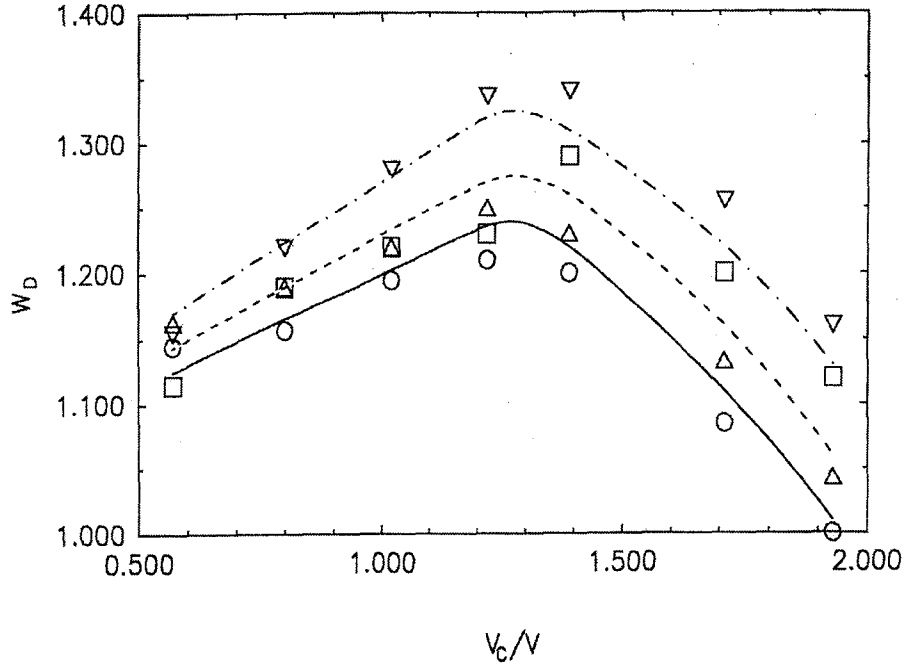

2.800
2.400
2.000
1.600
1.200
W_D
0.700
0.900
1.100
1.300
1.500
1.700
1.900
2.100
V_c/V

Figure 1:



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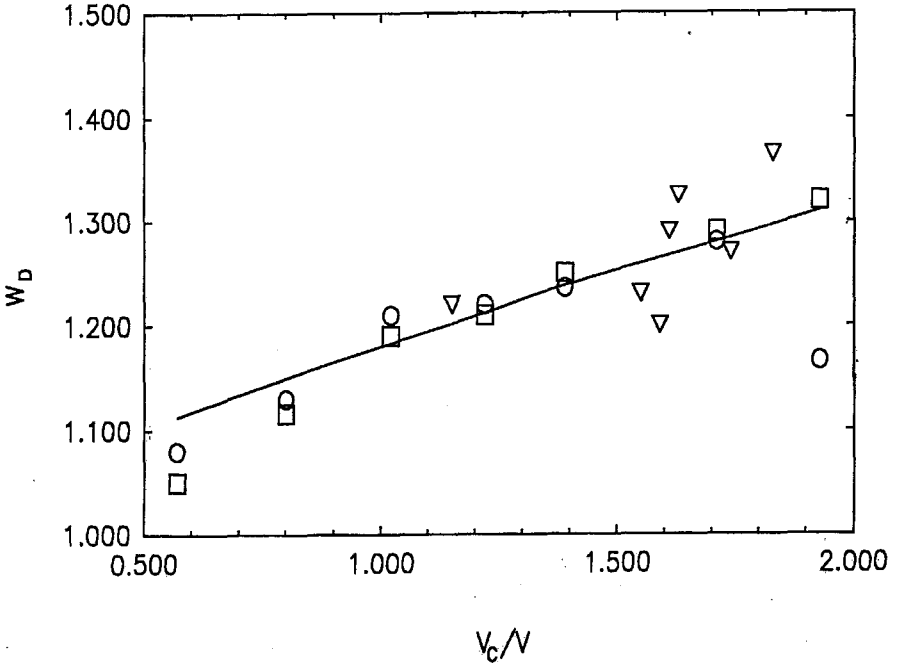
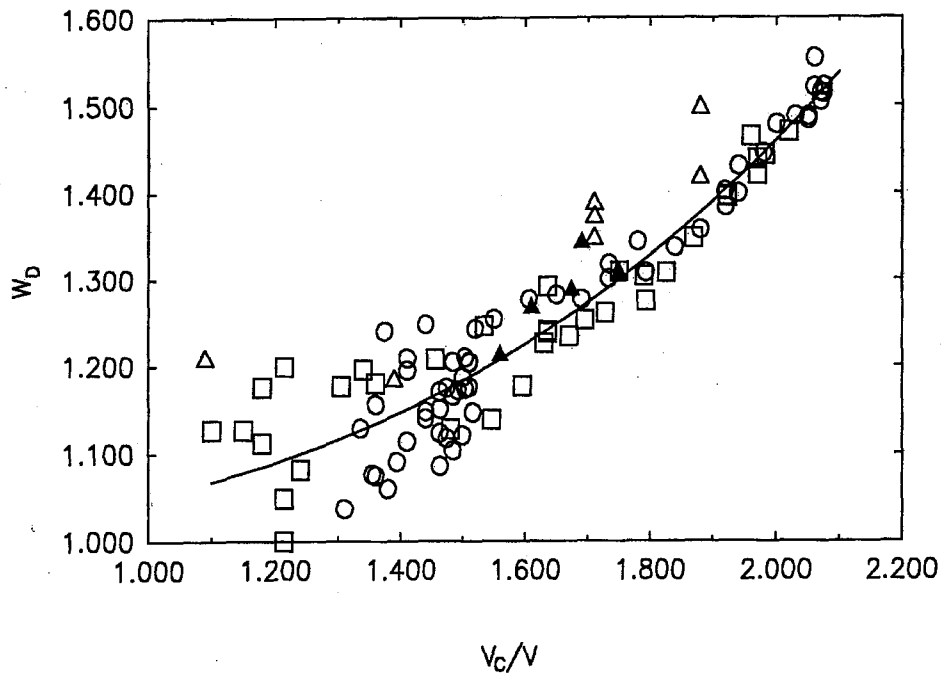


Figure 3: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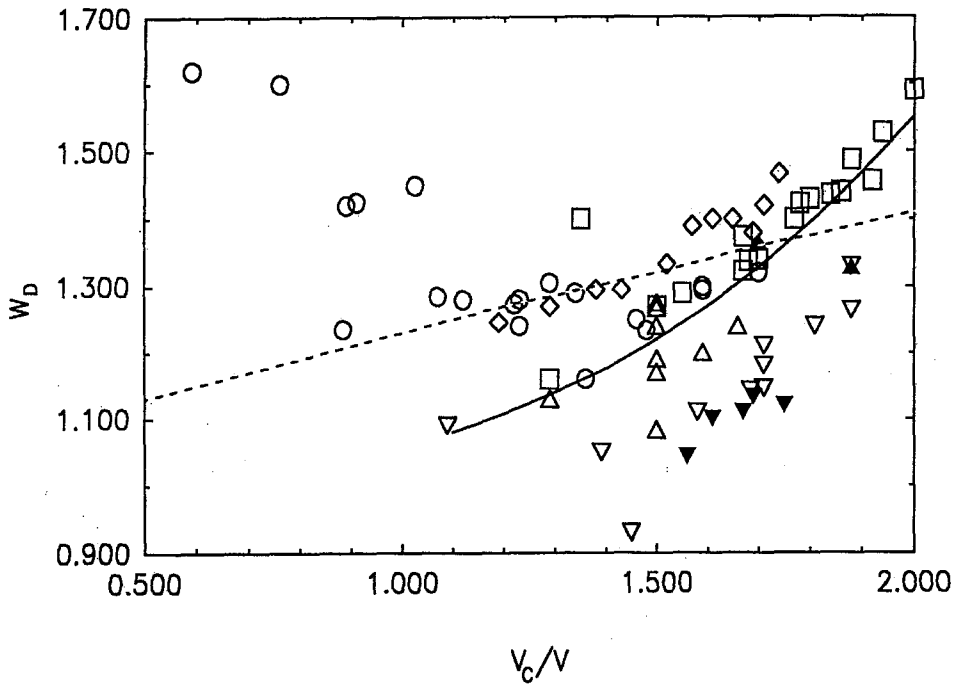
1.500
1.400
1.300
1.200
1.100
1.000
W_D
1.000
1.200
1.400
1.600
1.800
2.000
2.200
V_C/V

Figure 4:



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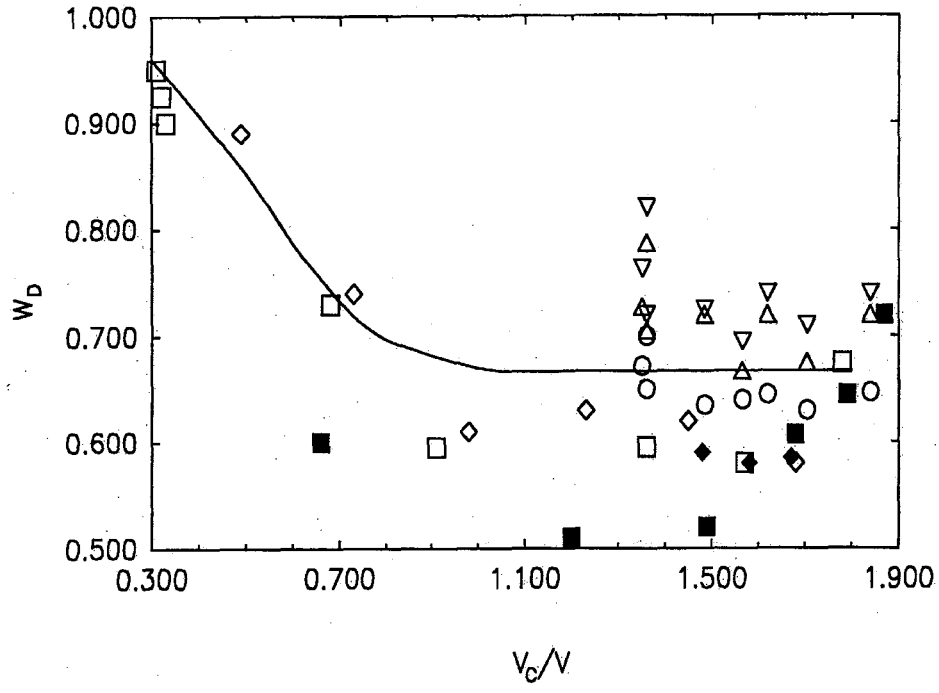

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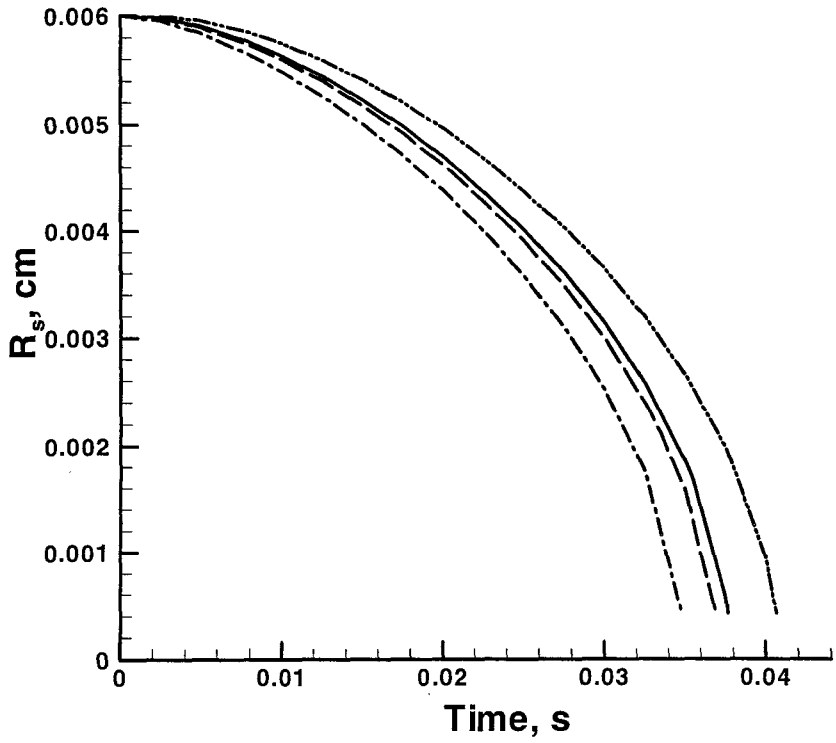

Figure 7: